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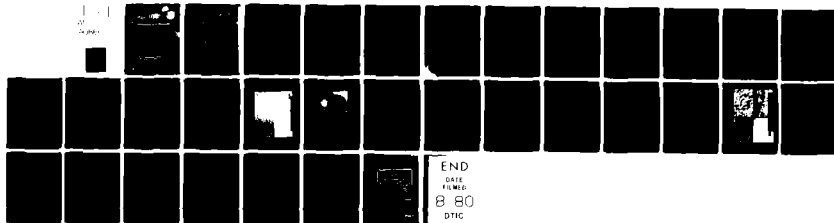
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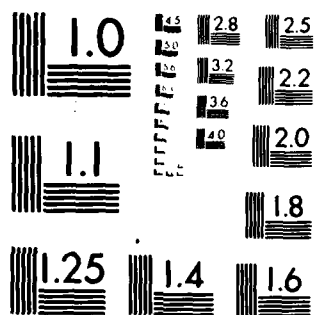
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SUMMARY

The growth of polycrystalline InP has been developed to the extent that high purity material can be reliably and reproducibly prepared in SiO_2 vessels from In solution at a growth rate of 2.5 cm/day. This represents an improvement of a factor of 2.5 compared with the state of development at the end of the first year. Further small improvements can be expected by optimization of the temperature gradient. Single crystal growth of InP is at a fairly advanced state as to the purity and defect density. Undoped crystals can be routinely grown having background carrier concentrations in the $10^{15}/\text{cm}$ range. Similarly, practically zero dislocation density crystals doped with S and Zn are routinely prepared. The purity and perfection of the crystals was determined by van der Pauw, low temperature photoluminescence and transmission x-ray topography measurements.

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PREFACE

Contributions to the research described herein were made by C. L. Wei in the growth of single-crystal InP, and by M. L. Simkins in the preparation of polycrystalline InP.

Previous and related contracts are as follows:

N00123-76-C-1312 and 0416: "InGaAsP for Infrared Applications," Naval Ocean Systems Command, CA, June 1976 to Aug. 1977.

DAAG29-76-C-0015: "Basic Improvements in Substrate InP Materials," Army Research Office, SC, February 1976 to January 1978.

The following article has resulted to date from the research accomplished on this contract:

D. Barthruff, K. W. Benz, and G. A. Antypas, "Photoluminescence Characterization of Solution and LEC Grown InP⁺," J. Electron. Materials 8, No. 4, 485-491 (1979).

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EVALUATION

InP has emerged as a highly promising semiconductor material for use as substrates in lattice matched integrated optics and high efficiency low noise signal processing devices. However, high quality indium phosphide single crystals from which suitable substrates can be obtained are very expensive and in extremely short supply in the world market.

As a result of this contract conditions for the reliable, reproducible synthesis of high purity polycrystalline indium phosphide, from indium solutions, by the horizontal Bridgman technique have been optimized. Using this technique 500 gram ingots have been synthesized in quartz ampoules. This polycrystalline InP is the highest purity material yet reported. Low temperature photoluminescence measurements show that the purity of this material is equivalent to high purity epitaxial grown InP. Undoped crystals grown by the liquid encapsulation Czochralski technique (LEC) were also the highest purity single crystals of InP reported. Conditions for the LEC growth of single crystals of indium phosphide either undoped or doped with iron, zinc, tin or sulfur were optimized. Crystals doped with zinc or sulfur have been grown with zero dislocations.

This was a very successful contract. As mentioned above, a reliable technique for the synthesis of high purity polycrystalline InP was developed and techniques for the LEC growth of doped and undoped single crystals were established. Problems which remain however are: 1) The synthesis technique is still slow. 2) A reliable technique for the elimination of twinning during LEC growth has not been found.



JOHN K. KENNEDY
Project Engineer

I. INTRODUCTION

InP is continuing to receive increased attention as a semiconductor that can form the basis for the development of microwave and optoelectronic devices. The present two-year program, along with programs funded by the Army Research Office and Advanced Research Projects Agency, have made possible the development of InP bulk growth technology capable of preparing not only high purity but also practically zero dislocation density crystals. These developments will play an important role in the commercial utilization of devices based on InP.

From the preparation point of view -- a major obstacle still exists -- that is the rapid synthesis of high-purity polycrystalline material. The problem originates from the high partial pressure of P over InP at the melting point (1062°C). Although commercial equipment is available for the rapid synthesis of InP at the stoichiometric point, the purity of the material prepared by such a process is limited to the 10^{16} - 10^{17} /cc range. Applications requiring highly doped substrates of n or p type can be satisfied by the use of this type of material. Applications, however, requiring either insulating or low-doped substrates require starting material of high purity that so far has been prepared only from solution. It is not clear, however, at this point whether increasing the temperature from 1040 to 1062°C for In and 460-540°C for P should have such a pronounced effect on the purity of the material.

II. POLYCRYSTALLINE GROWTH

During the first year of this program the basic process was established for the growth of polycrystalline InP from solution. In this Bridgman-type of process, the In temperature was controlled at 940°C, the phosphorus temperature controlled at 420°C, and the temperature gradient was 15°C/cm. Under these conditions, a growth rate of 1 cm/day could be maintained. Such a low growth process has its limitations when it is adopted to production environments. One obvious solution to increasing the growth rate is to increase the reaction temperature. Two factors have to be considered, however:

- a) The effect of the P pressure increase on the reliability of the process, and
- b) The effect of the increased reaction temperature on the incorporation of undesirable impurities.

In order to study both of these factors, a number of runs were performed having various P and In reservoir temperatures. Although the temperature gradient between In and P temperatures was not measured for each run, it is not believed to have changed markedly from the originally-measured value of 15°C/cm; it appears that this parameter would have little effect on the properties of the material, other than stoichiometry.

Table I shows the growth parameters and electrical properties of five representative polycrystalline runs. The In temperature varied between 940° and 1040°C, approaching the InP melting point of 1062°C, while the P reservoir temperature varied between 420° and 460°C yielding a P partial pressure

TABLE I

Growth and Characterization of Polycrystalline InP Ingots

Travel Rate cm/day	Run No.	In Temp °C	P Temp °C	Mobility cm^2/Vsec RT 77°K		$(N_D - N_A)/\text{cc}$ R_T 77°K	
1.0	1	940	420	5430	91000	6.9×10^{14}	6.9×10^{14}
1.0	2	980	430	5280	76700	8.5	8.0
2.5	22	1000	420	3780	60000	8.0	8.0
2.5	24	1020	420	4500	81000	9.0	6.0
2.5	25	1040	460	4750	86000	4.3	4.0

of 2.5-5.9 atm. The results shown in Table I are for data exclusively obtained from the first solidified section of the ingots. These sections typically have larger grain sizes and furthermore represent the background distribution of impurities in the absence of any accumulations or depletions of impurities associated with distribution coefficients greater or lower than unity.

All runs were made with In and P obtained from the same vendor. Materials and glassware cleaning was the same for all runs. All runs with the exception of run #22 yielded a material of similar background concentration and mobility. It is not clear at this point what was the cause of the lower mobility values obtained in this run, although the background carrier concentration was comparable to all other runs. Apparently the compensation ratio was higher. This can arise from a number of contamination sources, including original starting material, glassware used, charge preparation, and ampoule sealing. In any event, these results are extremely encouraging and point to the possibility that the process as developed here can potentially yield high purity polycrystalline InP at high growth rates. It should be pointed out that all the synthesis runs are made in SiO_2 boat and ampoules; and on the average, the background carrier concentration is at least a factor of three lower, and the 77°K mobility, a factor of three higher compared with the results reported⁽¹⁾ for materials synthesized by a similar process in pyrolytic BN boats and liners.

Although Ref. (1) reports an improvement in material purity for material synthesized in PBN compared to SiO_2 , this improvement may simply be related to their process rather than any inherent advantages of PBN over SiO_2 as a container for the growth of III-V compounds. Similar argu-

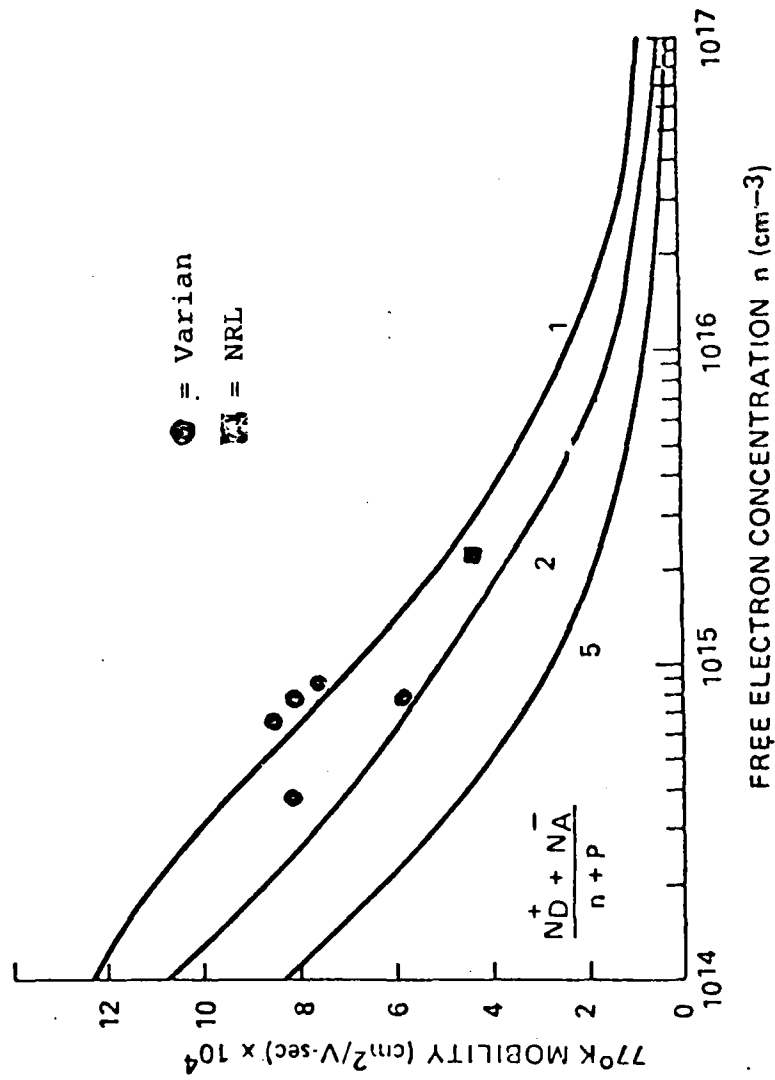


Fig. 1 77°K mobility vs free carrier concentration of samples shown in Table I. Best NRL result is also shown.

ments can be made for the growth of single-crystal InP by LEC in SiO_2 and PBN crucibles. Crystals grown at Varian and characterized by other laboratories, including Wright-Patterson Air Force Base and University of Stuttgart, by low-temperature photoluminescence and Van der Pauw measurements indicate that LEC InP single crystals produced in the Varian facility using SiO_2 crucibles typically have background carrier concentration of $1 \times 10^{15}/\text{cc}$ and 77°K mobility in excess of $50,000 \text{ cm}^2/\text{Vsec}$. These results represent the highest purity of InP single crystals so far reported.

Figure 1 shows the variation of 77°K mobility as a function of free electron concentration for various compensation ratios, theoretically calculated by Rode.⁽²⁾ Also shown on this figure is the best result reported by the NRL group for InP synthesized by PBN.

While increasing the reservoir temperatures to 460° and 1040°C for P and In respectively did not adversely affect the purity of the material, it allowed however the increase of the reaction rate by a factor of 2.5. At this point it is felt that with our present reactor design that the highest P temperature that can safely and reproducibly be achieved is 460°C. Under these conditions, a series of experiments were performed in order to determine the effect of travel rate. Run #30 was set up similar to Run #25 as to the charge size, heat-up cycle, and equilibration. The only difference being the travel rate which was increased to 5 cm/day. The non-stoichiometry of the charge at the end of the run as determined by the P that was incorporated in In was 24%. Van der Pauw measurements yielded fairly low results -- for the front portion of the crystal $\mu = 4150 \text{ cm}^2/\text{Vsec}$ and $N_D - N_A = 1.5 \times$

$10^{15}/\text{cc}$ at RT and $\mu = 30,100 \text{ cm}^2/\text{Vsec}$ and $N_D - N_A = 1.6 \times 10^{15}/\text{cc}$ at 77°K . This represents the lowest mobility obtained with MCP In and P starting material. It should be pointed out that the high nonstoichiometry of the charge could be responsible for these low results -- since although great care was taken to choose the Van der Pauw samples, it is possible that either grain boundaries or even inclusions could be present in the samples. In any event, while increasing the reaction temperature from 940°C to 1040°C for indium and 380°C to 460°C for phosphorus, we improved the material stoichiometry while still yielding high-purity polycrystalline InP in addition to allowing the increase of the reaction rate by a factor of two. Further increase of the reaction rate apparently cannot be obtained without further increase in temperature which could affect the reliability of the process. It is possible that a small increase in the reaction rate, on the order of 20-50%, could be achievable. It is certain, however, that a factor of 2 increase could not be obtained. This experiment effectively brings to a completion point the optimization of the InP synthesis process by horizontal Bridgman, which can be summarized as follows:

Bridgman InP Synthesis

In temperature	1040°C
P temperature	460°C
Temperature gradient	15°C/cm
Charge	475 gm
Reactor size	35mm dia x 100 cm - SiO_2
In boat	30 cm - SiO_2
Reaction rate	2.5 cm/day

III. Zn INCORPORATION

The process developed for the growth of polycrystalline InP provide efficient means of preparing extremely high-purity material in small quantities. The role of the purity in the starting material is dependent on the device application; almost without exception however, high device yields and long-lived operation of high current density devices, i.e., high radiance LEDs and lasers, normally demand low imperfection density substrates.

One of the main factors affecting the defect density of InP substrates has been the non-stoichiometry of the polycrystalline charge. The effect of the non-stoichiometry typically manifests itself in the form of inclusions in increasing density toward the last stages of growth. When initially starting with a non-stoichiometric charge, loss of P during single-crystal growth contributes to further deviations from stoichiometry, resulting in In inclusion and related defects. It has been reported, however, that the incorporation of Zn in InP results in reduced dislocation density.⁽³⁾ Such a relationship has been verified for Zn-doped InP grown at Varian, to the extent that effectively zero dislocation density material can be reproducibly prepared when $N_A - N_D > 1 \times 10^{18}/\text{cc}$. In addition to the reduction in dislocation densities, the inclusion density is reduced to zero even at the bottom of parts of the ingots. Since the solution non-stoichiometry is basically the same during growth of both Sn- and Zn-doped crystals, it is difficult to describe the effect of Zn in the reduction of dislocations and In inclusions. The model proposed by Seki et al⁽³⁾ is based on the Zn-P bond strength and although it can qualitatively explain the pinning of dislocations at the source -- such a source being the surface of the growing crystal -- it

cannot explain the growth of inclusion-free InP from non-stoichiometric solutions.

Figure 2 shows a comparison between a Sn-doped and a Zn-doped wafer, doped to the same doping level $\sim 1 \times 10^{18}/\text{cc}$. Figures 2(a) and (c) are optical photomicrographs of Sn- and Zn-doped (100)-oriented wafers etched in AB etch. In both cases, impurity striations arising from varying growth rates, particularly when the rotation center of the crystal is not coaxial with the thermal gradients. Such impurity striations are almost always present, in Czochralski-grown crystals, particularly when they are heavily doped. In addition to impurity striations, Fig. 2(a) shows extensive inclusion density. In general, the inclusions consist of numerous individual dislocations as shown in Fig. 3. This type of defect could have detrimental effects on the reliability, yield, and efficiency of devices.

Liquid phase epitaxy is extensively used in the fabrication of InP-based devices. A severe drawback affecting this technology is the substrate decomposition problem at relatively low temperatures in hydrogen environment. Since the problem is associated with the high phosphorus pressure over InP, a number of techniques have been used to suppress P loss. Such a technique is an In etch-melt, which typically removes few microns of the decomposed surface prior to growth. In Figure 2, photomicrographs (b) and (d) are representative surfaces of Sn- and Zn-doped InP, respectively. Again, it is obvious that the Zn-doped wafer is of far superior quality compared with the Sn-doped wafer.

In order to further elucidate the behavior of Zn in InP, an extensive series of experiments was initiated and although

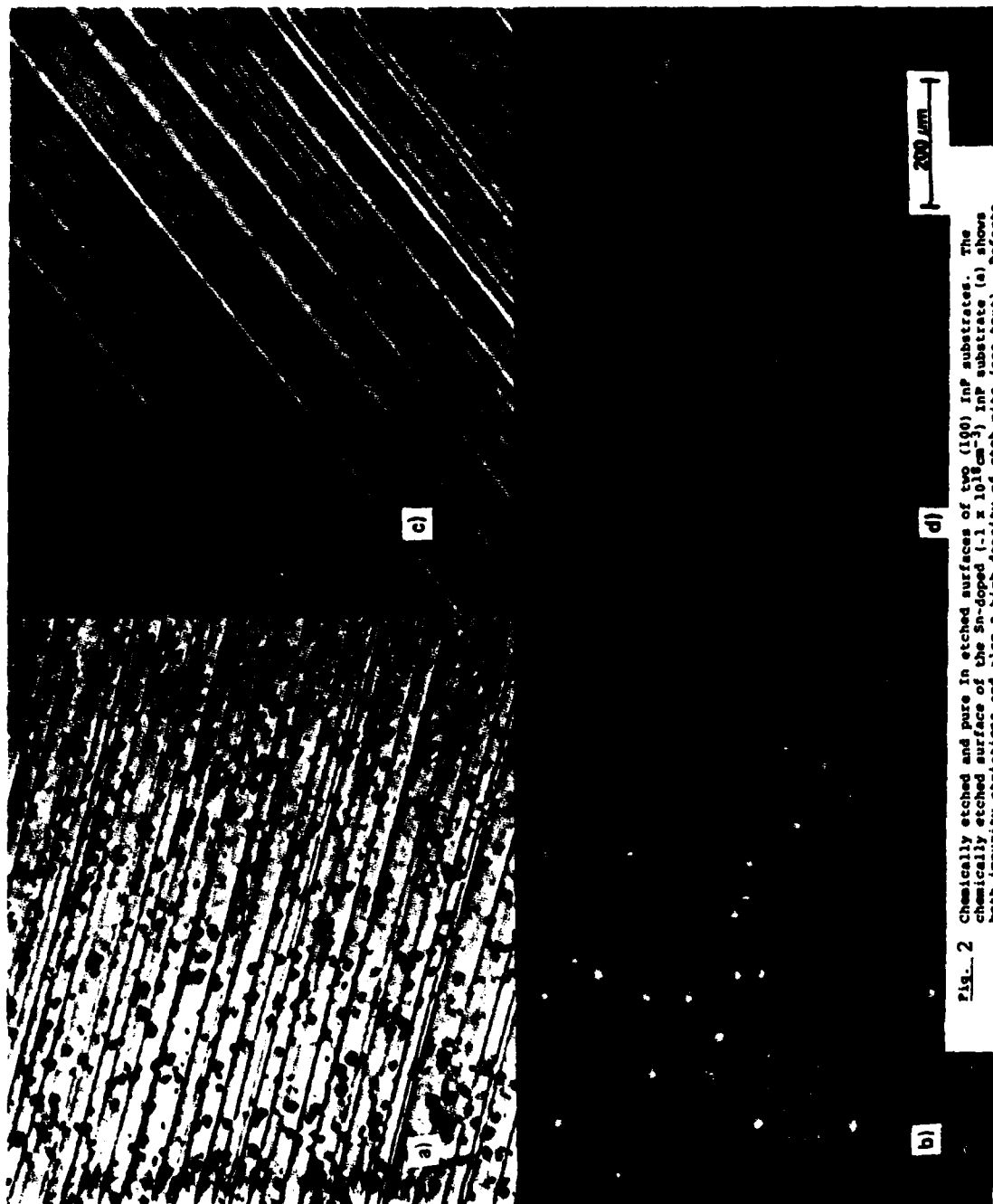


Fig. 2 Chemically etched and pure In etched surfaces of two (100) InP substrates. The chemically etched surface of the Sn-doped ($1.1 \times 10^{18} \text{ cm}^{-3}$) InP substrate (a) shows both impurity striations and also a high density of etch pits (see text). Defects in the Sn-doped InP substrate are preferentially etched by the pure In etch melt (b). The chemically etched Sn-doped ($1.1 \times 10^{18} \text{ cm}^{-3}$) InP substrate also shows impurity striations but very few etch pits are observed (c). The pure In etch melt smoothly etches the Sn-doped InP substrate (d).



Fig. 3. Cluster of dislocations close to a precipitate or an inclusion--etched with both $\text{HCl-HNO}_3\text{-Br}$ and $\text{H}_2\text{O}_2\text{-H}_2\text{SO}_4\text{-HF}$ etches.

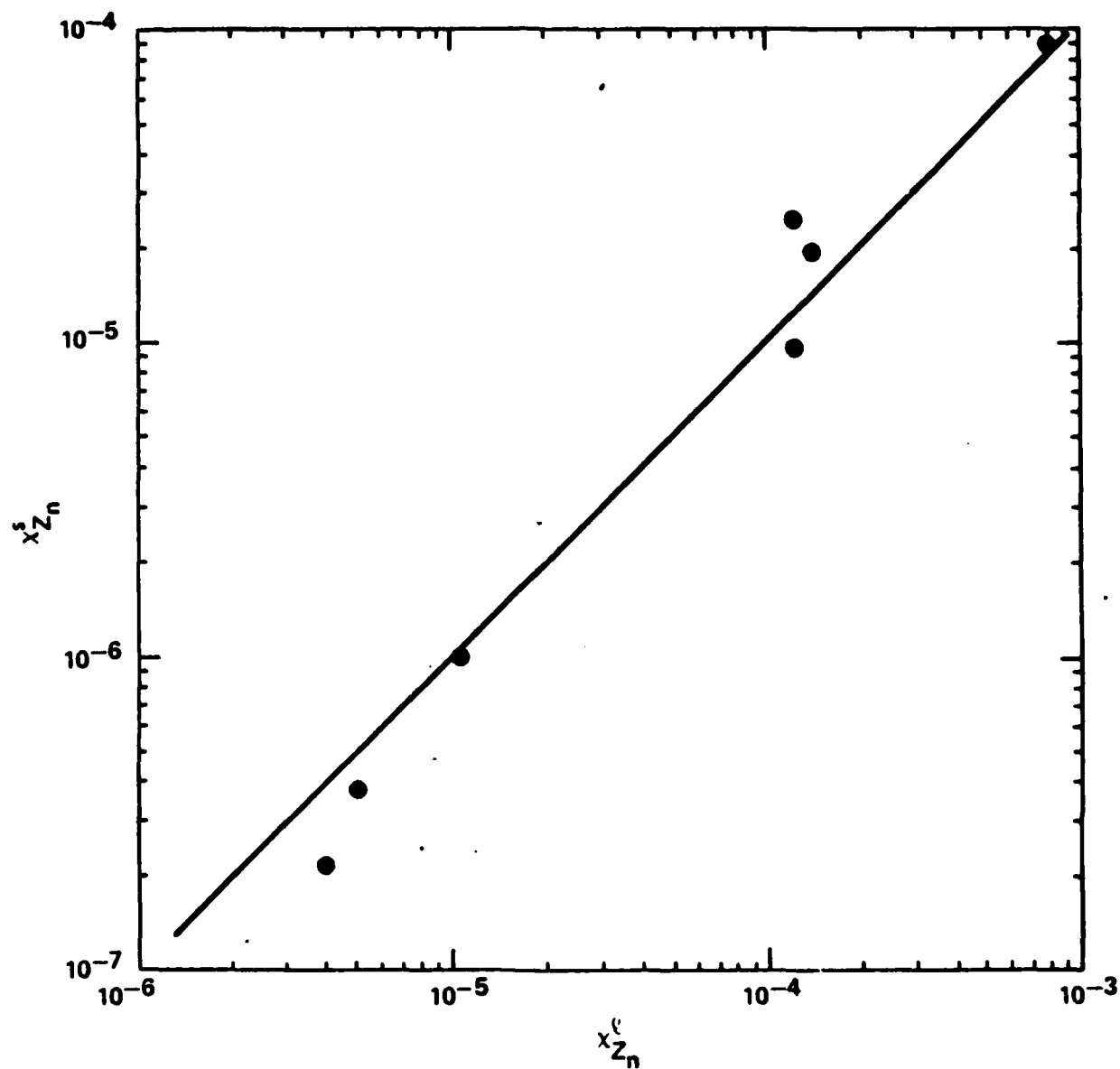


Fig 4. Distribution coefficient of Zn in LEC grown InP single crystals.

the study is not complete, the following conclusions can be made: (a) The incorporation of Zn in InP is associated with a reduction in dislocation and inclusion density, starting at $1 \times 10^{16}/\text{cc}$ and yields effectively zero dislocation and inclusion density at levels greater than $1 \times 10^{18}/\text{cc}$; and (b) the distribution coefficient of Zn in LEC-grown InP is ~ 0.1 , as can be seen in Fig. 4. A comparison of the photoluminescence spectra obtained at 77°K of high-purity undoped polycrystalline InP and slightly Zn-doped Inp $\sim 1 \times 10^{16}$ is shown in Figs. 5(a) and (b), respectively. In the undoped case the photoluminescence peak is at 1.4068, while for the p- sample the peak is at 1.4028. This difference of 4 mV is possibly associated with the energy difference of radiative decay of either free excitons or excitons bound to neutral donors and excitons bound to neutral acceptors. These transitions have been clearly resolved in photoluminescence measurements at 1.8°K on samples provided by Varian to Wright-Patterson Air Force Base and the Physikalische Institut at the University of Stuttgart, will be discussed in more detail in the next section. As the Zn concentration in the samples increases, the photoluminescence peak position shifts to lower energies in addition to the increase in their halfwidths. This non-destructive technique has been used qualitatively in GaAs in determining the carrier concentration in both n- and p-type material.⁽⁴⁾ Figure 6 shows the shift in photoluminescence peak position as a function of doping, for levels up to $4 \times 10^{18}/\text{cc}$.

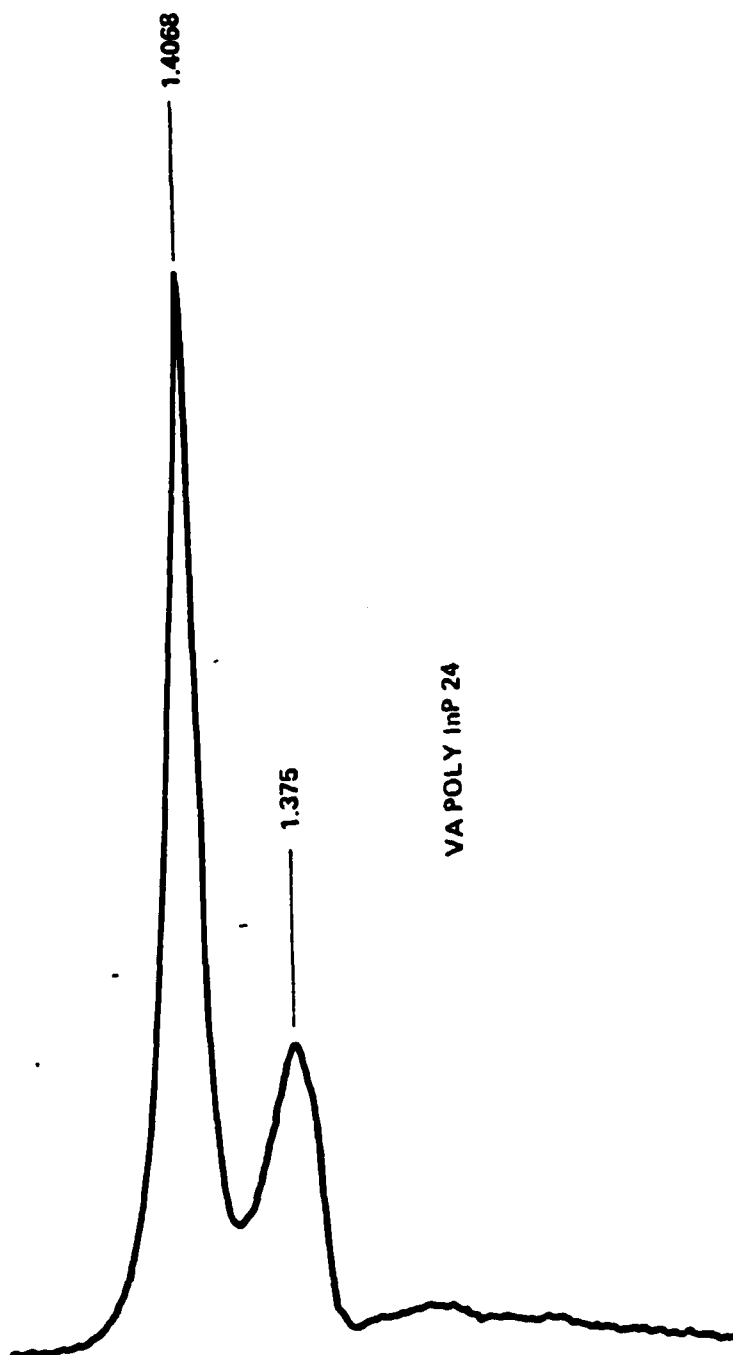


Fig. 5(a)

Fig. 5. Near bandgap photoluminescence spectra taken at 77°K of (a) high purity polycrystalline and (b) a low concentration ($\sim 1 \times 10^{16}/\text{cc}$) Zn-doped InP sample. Notice (1) the increased half-width of the Zn-doped sample, (2) the increased intensity of the peak at 1.375 associated with a donor-Zn acceptor transition, and (3) a shift in the near bandgap photoluminescence peak position to lower energies in the Zn-doped sample compared to the undoped sample.

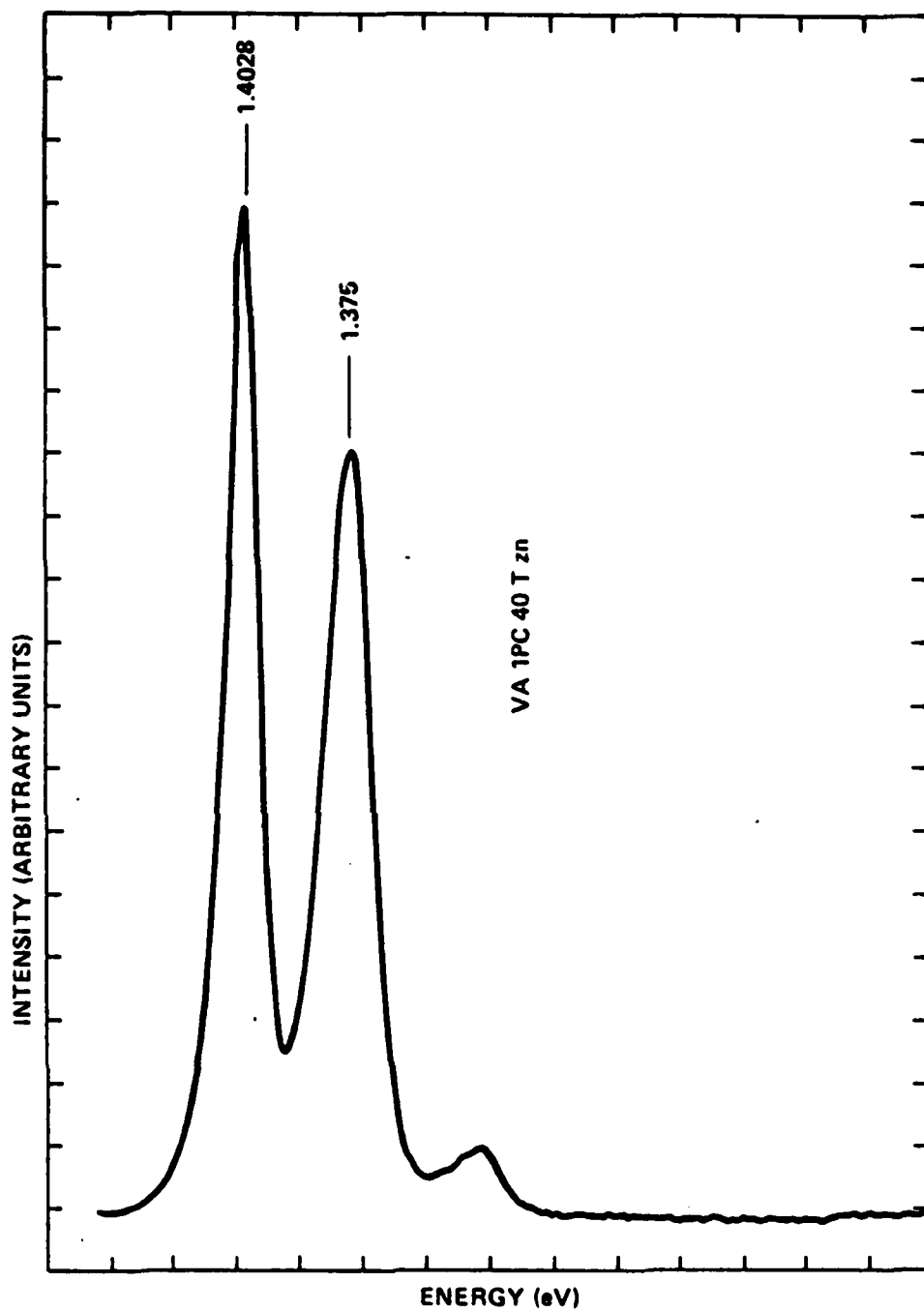


Fig. 5(b)

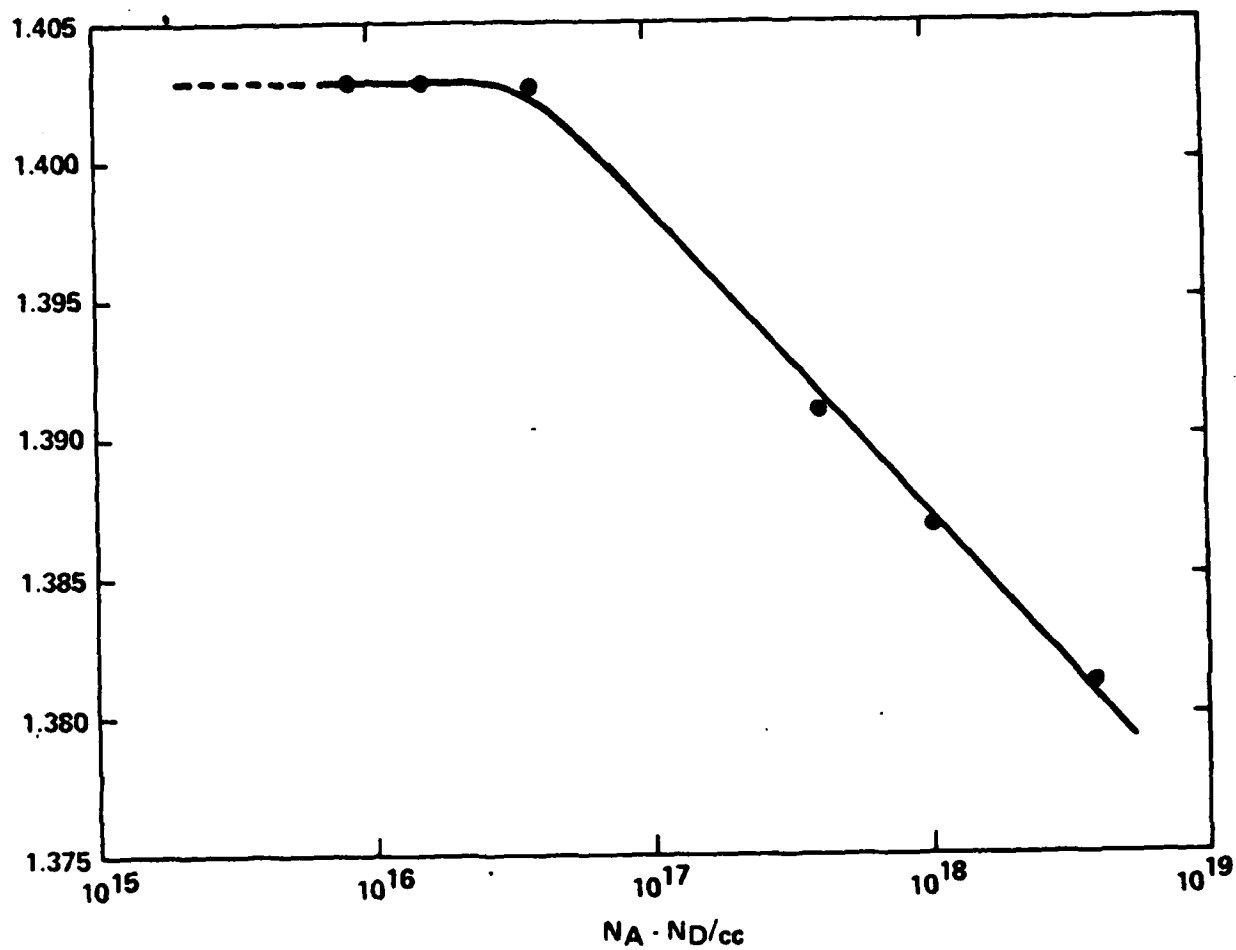


Fig. 6. The dependence of the 77°K near bandgap photoluminescence peak position on the Zn concentration in InP single crystals.

IV. MATERIALS CHARACTERIZATION

A. Transmission X-Ray Topography

In the previous section we described the growth of low-defect density highly-doped InP single crystals. The main characterization technique is optical photomicrography of etched wafers. X-ray topography, however, in both reflection and transmission mode, can provide basic information as to not only the defect density of the crystal but also the state of stress. In particular, when crystals are prepared at high pressures, the high convection cooling rate results quite often in built-in stresses that adversely affect device yields. Figure 7 shows transmission X-ray topographs obtained at RCA Laboratories of Sn, S, and Zn-doped InP crystals from wafers supplied by Varian. Figure 7(a) and 7(b) are topographs for 2×10^{18} /cc Sn-doped wafers, indicating a very high density of dislocation networks in addition to apparent precipitates or inclusions. Seki et al⁽²⁾ reported that the addition of a high concentration of certain impurities to the InP lattice results in dramatic reduction of the dislocation density. Such impurities include Zn and S. In both cases, when the concentration exceeds the 10^{18} /cc range, a sharp decrease in the dislocation density of LEC-grown InP crystals is observed. This effect was attributed to dislocation pinning at the source (the surface of the LEC-grown crystals) resulting from the higher bond energy between Zn-P and In-S compared with the In-P bond.

Our results appear to verify these conclusions. Figure 7(c) shows a transmission X-ray topograph from a (100) InP single crystal wafer which was doped with sulfur to a concentration of $\sim 4 \times 10^{18}$ cm⁻³. No dislocations were

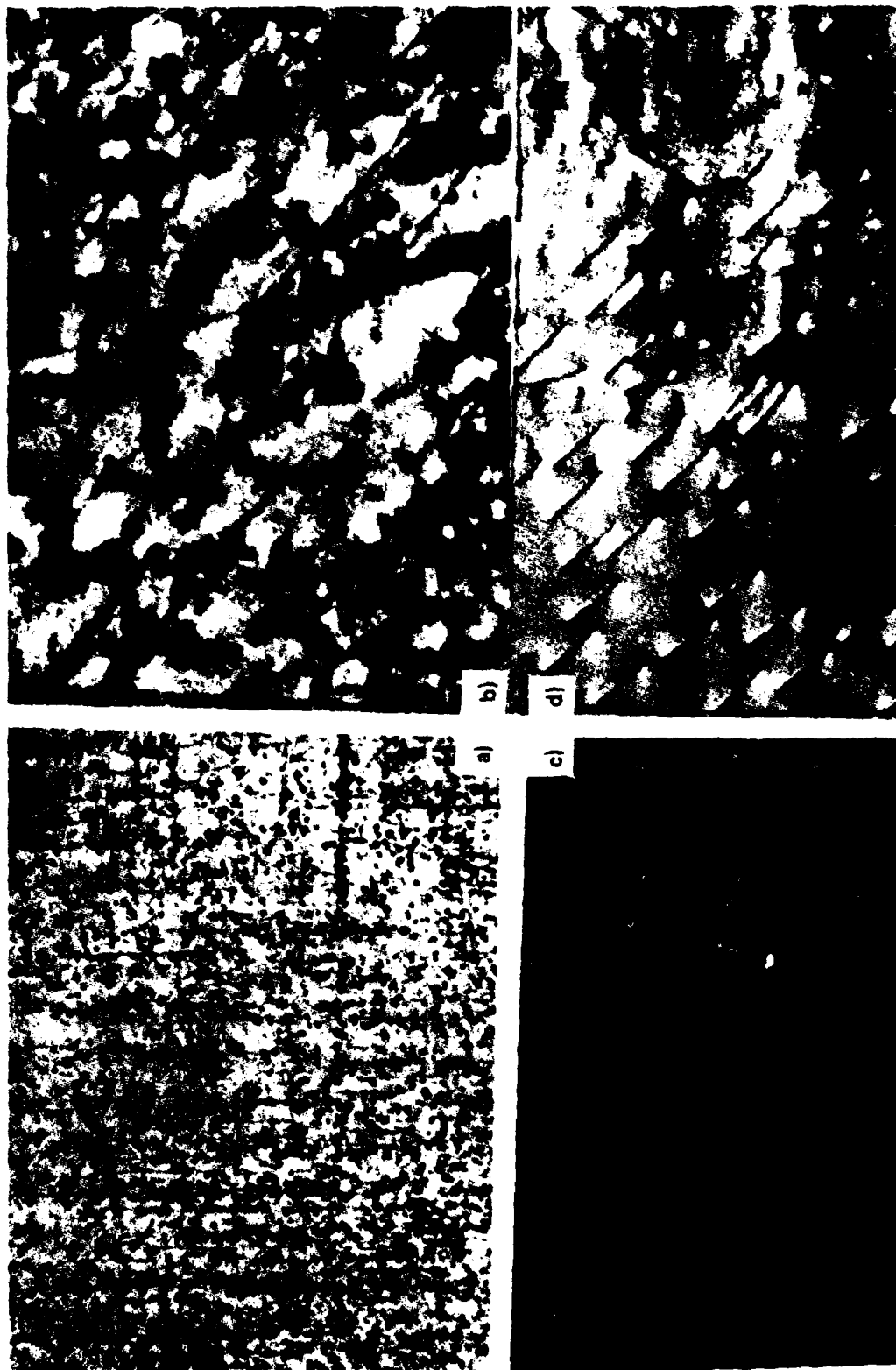


Fig. 7 Transmission X-ray topographs of low dislocation density InP wafers:

- a) Sn-doped $\sim 2 \times 10^{18}/\text{cc}$ c) S-doped $\sim 4 \times 10^{18}/\text{cc}$
 b) Sn-doped $\sim 2 \times 10^{18}/\text{cc}$ d) Zn-doped $2 \times 10^{18}/\text{cc}$.

observed anywhere across the wafer. Figure 7(d) is a transmission X-ray topograph from a (100) InP single crystal wafer doped with Zn to $1 \times 10^{18} \text{ cm}^{-3}$. A dislocation density of only $\sim 500 \text{ dislocations/cm}^2$ was measured. Contrast experiments determined that the dislocations were of the 60° -type as is commonly observed in most III-V compounds. Occasional twins and stacking faults could also be observed in this wafer. The low dislocation density could probably be reduced further by increasing the zinc content.

B. Low Temperature Photoluminescence

Low temperature photoluminescence characterization in InP has been limited to material prepared only epitaxially, either by VPE⁽⁵⁾ or LPE⁽⁶⁾. The recent development of high purity polycrystalline solution growth of InP under this and other related programs has provided the means for the growth of high-purity undoped InP single crystals by liquid encapsulation Czochralski (LEC). Table II summarizes the electrical properties of the samples that were chosen for low temperature photoluminescence experiments.

TABLE II

Results of Electrical Characterization

	<u>$\mu (\text{cm}^2/\text{V-sec})$</u>		<u>$(N_D - N_A)/\text{cc}$</u>	
	<u>300°K</u>	<u>77°K</u>	<u>300°K</u>	<u>77°K</u>
VAGF#2 (front)	5282	76680	8.5×10^{14}	8.1×10^{14}
(middle)	5870	85960	4.4×10^{14}	4.2×10^{14}
IPC#41	4664	52793	1.1×10^{15}	9.7×10^{14}

The crystals were excited by a He-Ne-laser ($\lambda = 632 \text{ nm}$), the maximum light density was $I_0 = 2 \text{ W/cm}^2$. The luminescence was resolved by a 1m-Jarrell-Ash monochromator and detected with a N-cooled photomultiplier (S_1 -characteristic) in connection with conventional lock-in techniques.

Figure 8 shows the emission spectra of various InP samples in the energy range of 1.37 eV - 1.42 eV. The photoluminescence of two solution grown samples (front end and middle section of the same growth run, curves a, b in Fig. 8) is compared to the emission of a LEC single crystal and a LPE layer (curves c, d in Fig. 8). The LPE layers were grown in a horizontal tipping system, which is described in detail by Fiochbach et al.⁽⁷⁾

The near-gap luminescence in Fig. 8 (energy range 1.41 eV - 1.42 eV) can be attributed to the radiative decay of free and bound excitons. The peak at 1.4183 eV has been identified as the free exciton-polariton emission,^(5,7) whereas the lines at 1.4149 eV and 1.4147 eV are related to excitons bound to neutral acceptors.^(5,7) The resolution of near-edge emission into these separate lines and their small half-width are a measure for the low impurity concentration in all crystals. Especially, the solution-grown samples (curve a, b in Fig. 8) depict a near-edge emission which is very similar to best LPE-layer (curve d in Fig. 8).

Band-acceptor-transitions (BA) and donor-acceptor pair bands (DA) can be resolved in the energy range between 1.37 eV and 1.39 eV. The transitions are correlated to $\text{Zn}^{(8)}$ - and C-acceptors.⁽⁷⁾ It can be seen from Fig. 8 that the Zn-acceptor is present in all crystals, whereas C has pronounced

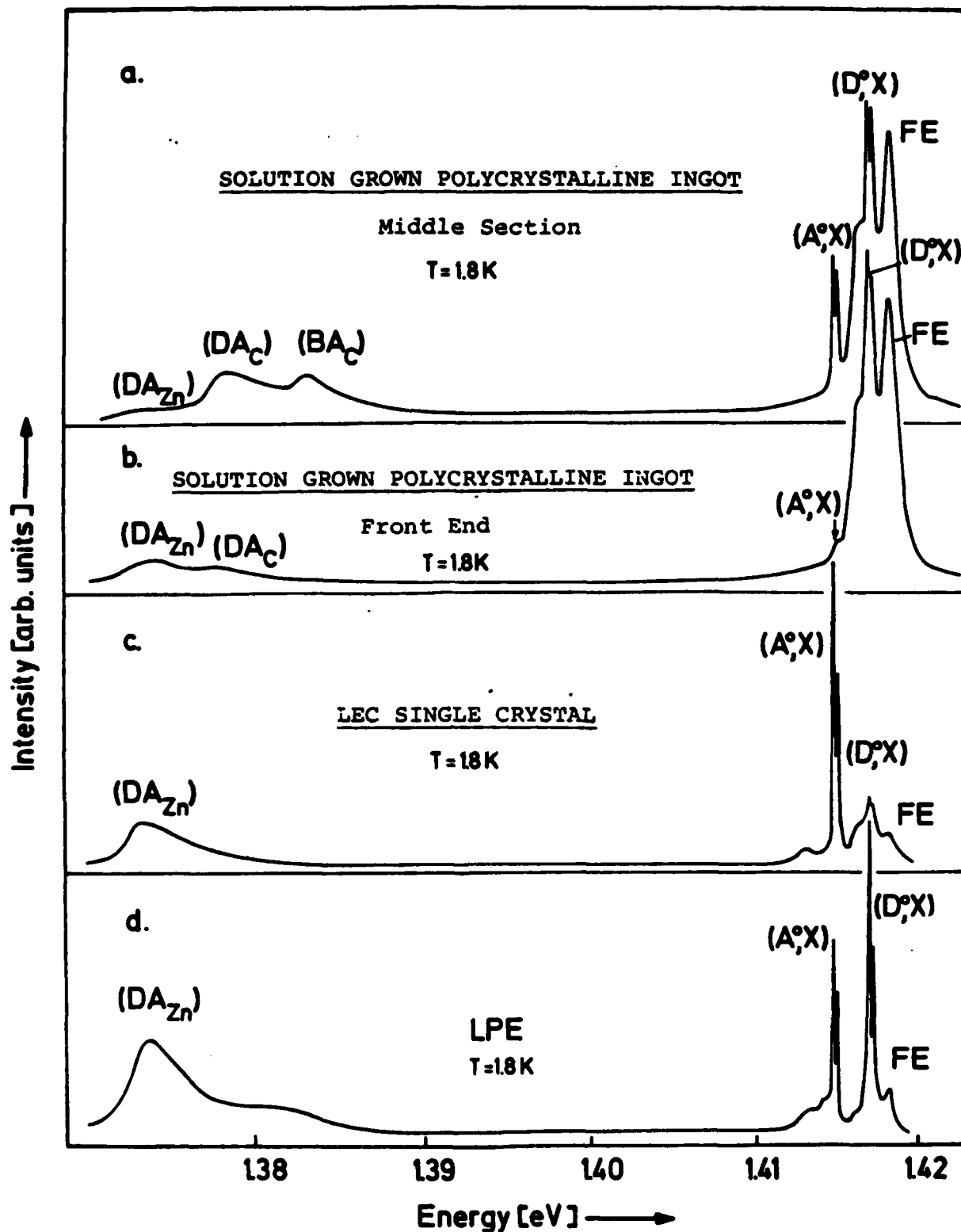


Fig. 8. Photoluminescence spectra of various InP samples in the energy range of 1.37 eV - 1.42 eV:

- a) Solution-grown polycrystalline ingot (middle section)
- b) Solution-grown polycrystalline ingot (front end)
- c) LEC single crystal
- d) LPE sample

emissions (DA_C) and (BA_C) in the middle section of the ingot. Comparable (DA_C) and (BA_C) emission lines can be detected in LPE-layers, especially at high temperatures.⁽⁶⁾

Figure 9 shows the emission spectra in the range of 1.29 eV - 1.37 eV of the solution-grown samples and the LEC crystal. Four new lines can be resolved in the photoluminescence spectra of the solution-grown samples (curve a,b) which cannot be seen in the case of the LEC crystal (curve c, Fig. 9) and LPE layers. The strong line denoted with α at 1.3612 eV is the dominant emission and may be interpreted as a decay of a bound exciton (due to its sharp half-width). The origin of lines β (1.3526 eV), γ (1.3423 eV), δ (1.3182 eV) is unknown. Recently Williams et al.⁽⁹⁾ reported on an emission line between 1.348 eV and 1.355 eV which was attributed to Cu-acceptor. The exact energetic position of this line depended on the preparation of the InP crystals.

For this reason line β may be assigned to Cu. Besides the no-phonon emission lines α , β , γ , δ , LO- and TO-phonons satellites can be seen in Fig. 9 (curve a,b).

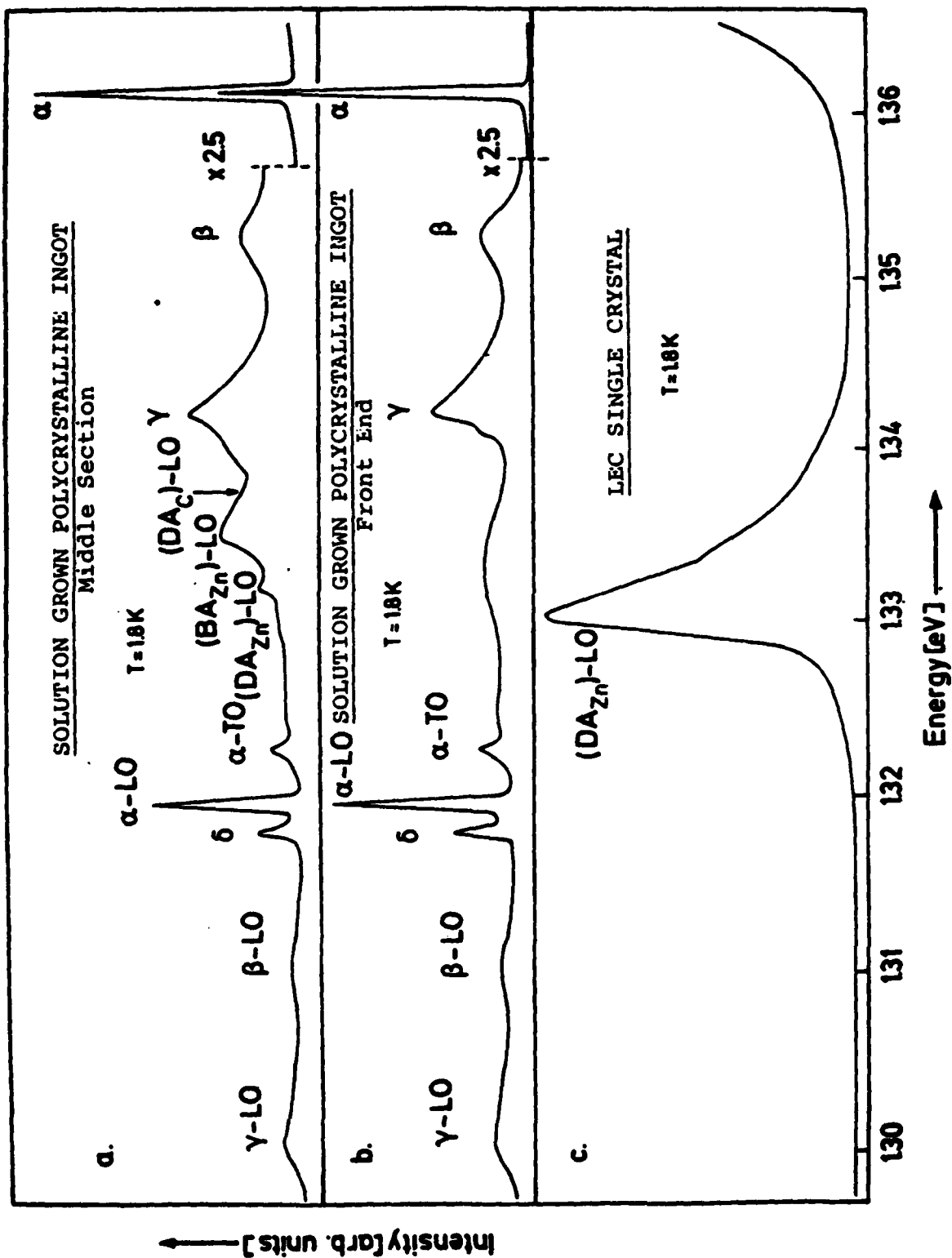


Fig. 9 Photoluminescence spectra of various InP samples in the energy range of 1.29 eV - 1.37 eV at 1.8 K:

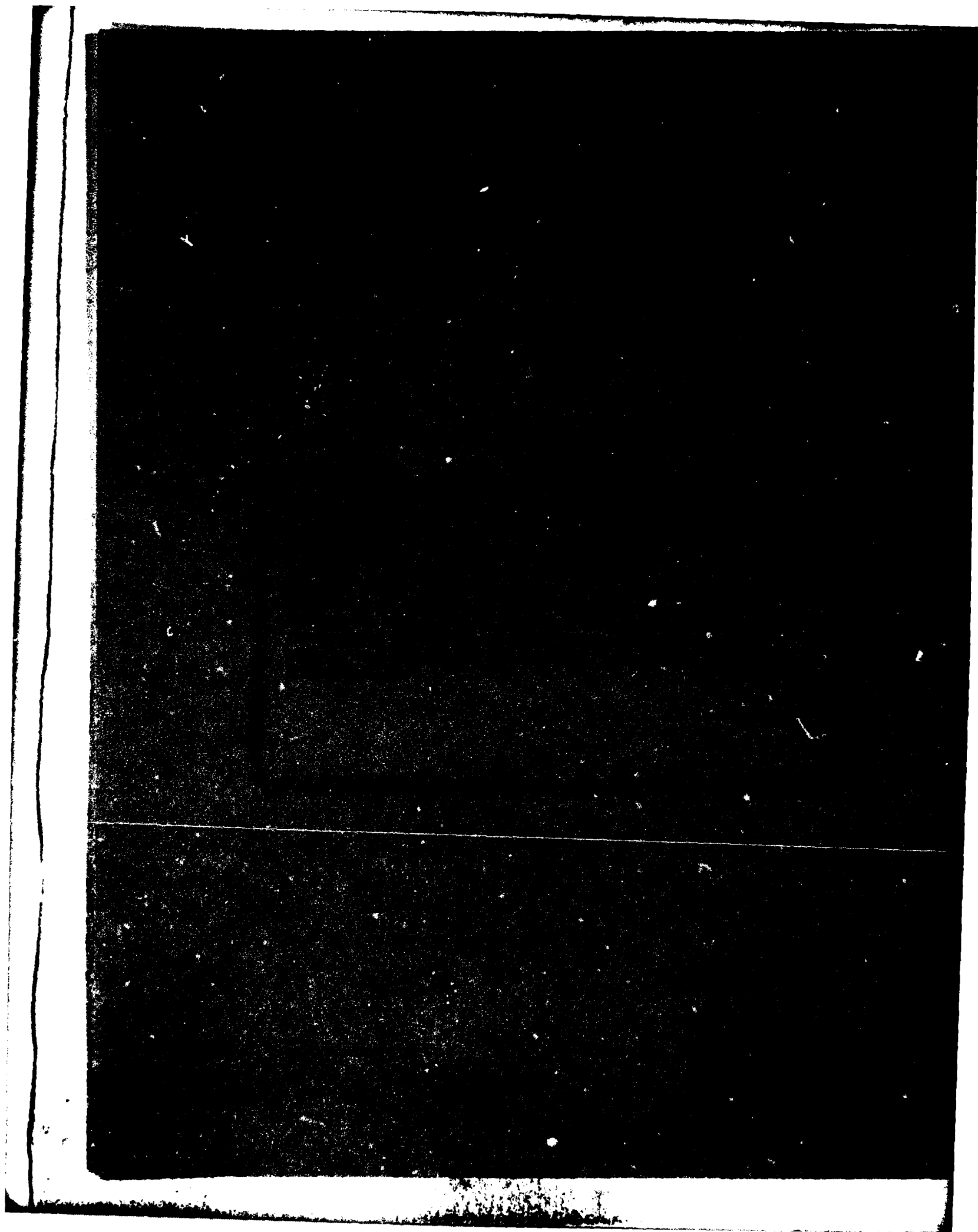
- a) Solution-grown polycrystalline ingot (middle section)
- b) Solution-grown polycrystalline ingot (front end)
- c) LEC single crystal

V. CONCLUSIONS AND RECOMMENDATIONS

InP has rapidly developed to a state where high purity and low defect density crystals can be routinely prepared. For that matter, we have shown that the purity of bulk single crystals is comparable to that of epitaxial growth based on van der Pauw and low temperature photoluminescence measurement. InP is the only bulk-grown III-V crystal that has demonstrated such a state of purity. In addition, practically zero dislocation density crystals can be prepared--again InP being the only III-V that can be bulk grown with such a low defect density. It should not be assumed, however, that bulk-growth InP technology has reached a level that will be able to supply the needs of a rapidly-emerging technology. The problems that still remain directly effect that availability of InP are slow growth rate of high-purity polycrystalline material, and high twinning probability of LEC-grown single crystals.

VI. REFERENCES

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